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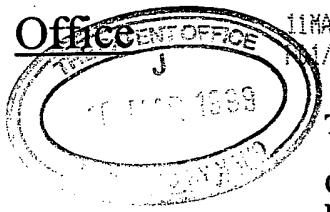

Request for grant of a patent

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1.	Your reference	JSnr/4750 GB/Deb 3
2.	Patent application number *(The Patent Office will fill in this part)*	**9905522.0** **10 MAR 1999**
3.	Full name, address and postcode of the or of each applicant *(underline all surnames)*	International Coatings Limited, 50 George Street, London, W1A 2BB, England
	Patents ADP number *(if you know it)*	7558026001
	If the applicant is a corporate body, give the country/state of its incorporation	United Kingdom
4.	Title of the invention	Powder Coating Compositions
5.	Name of your agent *(if you have one)* "Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*	Abel & Imray 20 Red Lion Street London WC1R 4PQ
	Patents ADP number *(if you know it)*	174001

6.	If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number	Country	Priority application number *(if you know it)*	Date of filing *(day/month/year)*

7.	If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application	Number of earlier application	Date of filing *(day/month/year)*

8.	Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:* *a) any applicant named in part 3 is not an inventor, or* *b) there is an inventor who is not named as an applicant, or* *c) any named applicant is a corporate body.*	Yes

9.	Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document.	
	Continuation sheets of this form	None
	Description	22
	Claim(s)	9
	Abstract	None
	Drawing(s)	None
10.	If you are also filing any of the following, state how many against each item.	
	Priority documents	
	Translations of priority documents	
	Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	
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		Signature: Abel & Imray ABEL & IMRAY — Date: 10/03/99
12.	Name and daytime telephone number of person to contact in the United Kingdom	JANET SENIOR — 0171-242 9984

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POWDER COATING COMPOSITIONS

FIELD OF THE INVENTION

This invention relates to powder coating compositions and to their use.

Powder coating compositions generally comprise a solid film-forming resin, usually with one or more colouring agents such as pigments, and optionally they also contain one or more performance additives. They are usually thermosetting, incorporating, for example, a film-forming polymer and a corresponding curing agent (which may itself be another film-forming polymer).

The compositions are generally prepared by intimately mixing the ingredients (including any colouring agents and performance additives) for example in an extruder, at a temperature above the softening point of the film-forming polymer(s) but below a temperature at which significant pre-reaction would occur. The extrudate is usually rolled into a flat sheet and comminuted, for example by grinding to the desired particle sizes ("micronising"). The size distribution required for most commercial electrostatic spray apparatus is up to 120 microns, often between 10 and 120 microns, with a Dv.50 within the range of 15 to 75 microns, preferably 25 to 50 microns, more especially 20 to 45 microns.

BACKGROUND TO THE INVENTION

Currently, powder coating manufacturing methods allow the manufacturer to offer commercially a range of full gloss coatings in a variety of colours. The range of products available in reduced-gloss finishes is, however, limited.

Reduction of gloss to some other lower level, for example satin gloss (55-65% gloss) or matt (< 30% gloss), is achieved by creating a surface which is rough on a microscopic scale. This may be achieved by using incompatible components or components that generate incompatibility. For example, an acrylic component and a polyester, epoxy, polyester-epoxy or polyurethane component are incompatible, and cannot be blended to form a single (stable) phase. Incompatibility during film formation can also be achieved by using components that are initially miscible (compatible) but that become incompatible during curing. Thus, for example, two systems of similar chemistry and approximately the same gel time are compatible, but components with different gel times are initially compatible but become incompatible as curing (and molecular weight build-up) proceeds. Thus, gloss-reducing agents include a second catalyst which will give a much faster gel time than the principal catalyst used to cure the film. Alternatively, with acid-functional polyesters, for example, a fast gelling (reacting) powder and a slow gelling powder may be manufactured separately using polyesters of different functionality, and mixed after the micronising stage or, more usually, the components are mixed prior to micronising; the components should have the same colour and particle size. Production of small batches of reduced-gloss coating composition, however, is uneconomic. A different method utilises a product called 'gloss killer', available from the company Tiger, which is mixed in after the micronising stage. However, this product, a clear (uncoloured) powder coating, can be added only in limited amounts to a conventional coloured powder coating before the presence of the gloss killer can be detected from the sparkle generated by the particles of the clear gloss killer powder in the film. Therefore the product is limited to adjusting gloss by a few percentage points.

There is accordingly a need for powder coating compositions in a wid range of reduced-gloss finishes, which avoid the problems mentioned above.

Speed of delivery to customers is also an important consideration, but the conventional powder coatings manufacturing method relies on premixing, extrusion and milling as separate processes, causing turnaround times to be long, and production of small batches of a product is again not economic. Stocking large product ranges solves the problem of speed of delivery, but is a highly inflexible approach and is not cost-effective.

EP 372860 A describes a colour mixing process for powder coatings in which sufficiently small-sized particles (< 20 μm in size and advantageously < 10 μm) are used that mixed colours applied to a substrate have a homogeneous appearance. Before application to the substrate the mixture is generally subjected to a process of agglomeration in which the small-sized particles are fused or bonded into composite particles, for example by mechanofusion, to convert the mixture from a cohesive mass to a free-flowing and fluidisable powder, which can be applied by conventional means. Thus, a range of basic coloured powder coating compositions is produced, conventionally, in a conventional melt extrusion step, and the products are comminuted to a distinctively small particle size. A range of other colours can then be produced by mixing and agglomerating these coloured powder bases in the desired proportions. This allows the storage of comparatively few basic coloured powder bases, which can be mixed and agglomerated to produce any desired shade easily on demand, and the production of small quantities becomes commercially feasible.

An extension of this agglomeration technique for the flexible production of a range of coloured powder coatings with a range of different reduced-gloss and other aesthetic effects is described in EP 539385 A.

Gloss reduction is achieved, for example, by adding uncoloured incompatible particles of mean particle size < 5μm, or initially compatible particles of mean particle size <20μm of a polymer having a different functionality from the polymer of the main

film-forming component. Amounts of the gloss-reducing agent are, for example, 5 or 10% by weight, although amounts up to 40% by weight are also disclosed.

SUMMARY OF THE INVENTION

The present invention provides a powder coating composition in which powder particles are an agglomerate of individual particulate components fused or bonded together into composite particles, wherein the individual particulate components comprise

- two or more coloured film-forming base components having a Dv.99 of no more than 30μm, and
- one or more uncoloured film-forming components having a higher Dv.99,

wherein

the specified uncoloured film-forming component(s) have a Dv.99 of more than 20μm and up to 40μm, the ratio of coloured film-forming base components to uncoloured film-forming component(s) in the composition being in the range of from 1:99 to 30:70, for example from 2:98 to 30:70, by weight, or

the specified uncoloured film-forming component(s) have a Dv.99 of more than 40μm and preferably have a Dv.99 of no more than 90μm, the ratio of coloured film-forming base components to uncoloured film-forming component(s) in the composition being in the range of from 1:99 to 60:40, for example from 2:98 to 30:70, by weight.

As will be understood in the art, the volume percentiles Dv.x indicate for a stated particle size (D) the percentage (x) of the total volume of the particles that lies below the stated particle size. Thus, for instance, Dv.50 is the median particle size of the sample, and on a particle size distribution graph Dv.99 is the point on the curve read along the particle size axis where the area under the curve below this particle size

represents 99% by volume of the particles. Thus, Dv.99 = 30μm indicates that 99% of the particles are below 30μm (but are not below 29μm). (For the avoidance of doubt, it should be noted that *all* particle sizes quoted herein are by volume.) Volume percentiles are measurable by laser diffraction techniques, for example by the Malvern Mastersizer.

Surprisingly, even with a high proportion of uncoloured component of significantly larger particle size than the coloured base components, nevertheless the particles of the larger-sized component are not visible to the naked eye, so that the composition gives the appearance of a single colour.

The coloured base components comprise colouring material and film-forming polymer. Thus, for example, they may be constituted as powder coating compositions in their own right, containing the usual powder coating additives, but having the specified (reduced) particle size.

An uncoloured film-forming component is usually also a powder coating composition in its own right, but having the specified particle size; this component should have a higher Dv.99 than the coloured film-forming base components, preferably a Dv.99 of at least 40μm, for example in the range of from 50 to 65μm. Preferably it will have a Dv.90 of no more than 75μm and advantageously will have a mean of at least 8μm, especially in the range of from 12 to 30μm. The uncoloured film-forming components have the advantage of lower manufacturing cost in relation to the small-sized coloured components and their use allows easy adjustment of the polymer/ pigment ratio in the composition.

The present invention also provides a kit comprising the following separate components for agglomerating into powder coating compositions for the preparation of powder coatings in a number of different finishes:

- a plurality of coloured film-forming base components, each with a Dv.99 of no more than 30μm, and
- one or more uncoloured film-forming components having a higher Dv.99, of more than 40μm and preferably no more than 90μm.

Such kits allow a rapid and flexible manufacture of a range of coloured powder coating compositions, reduced-gloss finishes being manufactured by the use of an uncoloured component that is incompatible with the coloured base component or that becomes incompatible therewith during film-formation.

DETAILED DESCRIPTION OF THE INVENTION AND DESCRIPTION OF PREFERRED EMBODIMENTS

More especially, the present invention provides a powder coating composition, suitable for providing a coating having certain appearance or performance attributes, which comprises composite particles formed by the agglomeration of individual particulate components fused or bonded together into composite particles such that the composite particles are air-fluidisable and can be applied to a substrate by electrostatic spray without causing the individual particles in the composite particles to break down under the mechanical and/or electrostatic forces associated with their application to a substrate, wherein the individual particulate components comprise two or more coloured film-forming components having a Dv.99 of no more than 30μm and one or more uncoloured film-forming components having a higher Dv.99, of more than 20μm, and preferably of no more than 90μm, the ratio of said coloured film-forming base components to said uncoloured film-forming component(s) being in the range of from 1:99 to 30:70, by weight, or, where the uncoloured film-forming component(s) have a Dv.99 of more than 40μm, the ratio of said coloured film-forming bas components to

said uncoloured film-forming component(s) being in the range of from 1:99 to 60:40 by weight, each particle of each film-forming component comprising a solid polymeric binder system at least a portion of which is a film-forming resin, the resin in the composition being in an amount sufficient to impart film-forming properties to the composition.

Each film-forming component of the composition comprises at least one solid film-forming resin and includes any curing agent required therefor, and is usually formed by an extrusion process and comminution to the requisite particle size. Where a film-forming component is coloured, the colouring agent or agents (pigments and/or dyes) is (are) generally extruded with the film-forming resin(s), plus any curing agent, so that particles formed therefrom comprise film-forming resin, colouring agent and, where applicable, curing agent.

Film-forming components of similar chemistry but different gel times provide incompatibility during film-formation, and reduction in gloss may be achieved by such means using, for example, an uncoloured film-forming component having a different functionality from the coloured film-forming base components and optionally also containing a different catalyst (both of which lead to different gel times). For example, coloured and uncoloured components may be based on polyesters of different functionality. For polyurethane systems using hydroxy-functional polyesters cured with an isocyanate (typically isopherone diisocyanate), hydroxy-functional polyesters with radically different functionality may be used, e.g. a hydroxy-functional polyester with a functionality of 7 for an uncoloured component and one with a functionality of 2 used for the coloured base components. Another possibility is to employ polymeric materials that are *per se* incompatible with each other, for example a polyester and an acrylic polymer.

In contrast to conventional prior art gloss-reduction processes, which generally use 50:50 non-fused mixtures of same-sized powders, with fused or bonded

compositions of the present invention good gloss reduction can be achieved with substantially different proportions of gloss-reducing additive. The agglomerated material also does not suffer from particle segregation in the solid state as would dry-blended product, thus giving uniformity of product even after transportation and spraying.

In comparison with agglomerated coloured powder coating compositions described in EP 372860 A and EP 539385 A, compositions of the present invention contain a high proportion of uncoloured film-forming component, and the individual coloured components necessarily contain a significantly higher content of pigment. Moreover, the particle size of the uncoloured particles can be significantly larger than those of the coloured base components, without, surprisingly, affecting visual homogeneity. Thus, contrary to expectation and contrary to the suggestions in EP 372860 A and EP 539385 A, powders containing significant quantities of uncoloured component(s) having a Dv.99 >40μm can be used to produce powder coating films in which the differences between the coloured particles and the uncoloured particles are not discernable by the unaided human eye. Maximising the level of larger-sized uncoloured component(s) will give cost advantages.

Moreover, uncoloured components can be used for extension of product ranges, not only for giving different finishes, but also, by using different chemistries, for giving different performance characteristics. The different chemistries may arise, for example, from the use of different film-forming polymers, e.g. polyester and acrylic or polyester and epoxy, but may also arise from the use of different curing agents, e.g. polyester with an epoxy curing agent in one component and polyester with a bis(beta-hydroxyalkylamide) curing agent such as PRIMID in another component.

An uncoloured film-forming component of a kit of the invention may be a pre-prepared uncoloured coating composition of the specified particle size or one of

conventional size which is reduced in size just prior to use. Advantageously, for any particular type of film-forming chemistry (e.g. acid-functional polyester, hydroxy-functional polyester), a kit of the invention includes a "universal" gloss-reducing component suitable for all powder coating compositions of that chemistry. The present invention has the advantage of reducing costs while also reducing stocking levels and manufacturing capacity. It enables a very rapid and flexible service to be provided cheaply to the customer, allowing for the possibility of providing small quantities of powder coating compositions economically on request.

Advantageously, the coloured film-forming base components taken together contain at least 5%, e.g. at least 10%, and usually up to 70%, e.g. up to 60%, by weight of pigment, calculated on the total weight of these components. Advantageously, each contains at least 8% by weight of pigment, calculated on the weight of that component. The number of coloured film-forming base components may be, for example, at least 7, e.g. in the range of from 7 to 30.

Examples of pigments which may be used in the coloured base components are inorganic pigments, such as, for example, titanium dioxide white, red and yellow iron oxides, chrome pigments and carbon black, and organic pigments such as, for example, phthalocyanine, azo, anthraquinone, thioindigo, isodibenzanthrone, triphendioxane and quinacridone pigments, vat dye pigments and lakes of acid, basic and mordant dyestuffs. Dyes may be used instead of or as well as pigments. Each coloured base component of the coating composition may contain a single colorant (pigment or dye) or may contain more than one colorant. Where appropriate, a filler may be used to assist opacity, whilst minimising costs.

Additional pigment may alternatively be added as a separate component prior to agglomerating, especially if the pigment is close in colour to the mixed coloured film-forming base components. Any pigment added in this way would generally be up to 3%, preferably up to 1%, by weight, based on the weight of the total composition,

although amounts up to 5% may also be possible. Thus, for example, pigment in an amount of up to 3% by weight, more especially up to 1% by weight, may be used to displace the colour of the components over a small colour region, this being used for colour tinting or colour correction of a batch.

Preferably, the total weight of pigment in the composition is at least 0.5%, more especially at least 5%, and preferably no more than 30%, although an amount up to 50% is potentially also possible.

One or more other components may also be present. Other optional components include, for example, performance and aesthetic additives mentioned in EP 539385 A or those additives combined in a masterbatch with uncoloured film-forming polymer, often itself constituted as a powder coating composition in its own right, the masterbatch being prepared, for example, by co-extrusion of polymer and additive, followed by comminution, or by agglomeration of the particulate additive with uncoloured film-forming powder. Such further aesthetics component may be present for example in an amount of from 0.5 to 50% by weight of the total composition. A non-film-forming performance component is generally present in an amount of no more than 5% by weight of the composition, e.g. in an amount of from 0.5 to 5% by weight. Where such other component(s) are present in a composition of the present invention, the amounts of the specified coloured film-forming base components and/or the specified uncoloured film-forming component(s) in the composition may be altered accordingly.

A composition of the present invention may contain, for example, at least 1%, e.g. at least 2%, often at least 5%, by weight of the specified coloured film-forming base components, and usually there will be at least 20%, e.g. at least 30% or at least 40%, by weight of the uncoloured film-forming component of th size specified above. Preferably, the content of uncoloured film-forming component(s) is at least 40%, e.g. at least 50%, and advantageously at least 60%, and preferably at least 70%, by weight.

Amounts of at least 40% e.g. at least 50%, and advantageously at least 60%, and preferably at least 70%, by weight of uncoloured film-forming component(s) of the size specified above should especially be mentioned.

Ratios of from 1:99, e.g. from 2:98, preferably from 5:95, and up to 60:40, e.g. up to 50:50, advantageously up to 40:60 and preferably up to 30:70, for the coloured film-forming base components to uncoloured film-forming component(s) of the specified size or for coloured film-forming base components to total uncoloured film-forming components should especially be mentioned.

Preferably, in each of the coloured film-forming base components all the component particles are <25μm, and advantageously no more than 3% of component particles are <1μm. Advantageously the components have at least 90% by volume of particles < 20 microns, more especially at least 90% by volume < 10 microns and advantageously the components have a Dv.99 of at least 6μm, advantageously up to 25μm. Advantageously, the mean particle size of each such component is up to 18μm, preferably up to 15μm, e.g. up to 12μm, advantageously at least 2μm, for example within the range of for example 2 to 8μm, preferably 2 to 6μm or 8 to 12μm; mean sizes ≥3μm and ≤5μm should especially be mentioned.

A coloured film-forming base component of a kit of the invention may, however, be of larger particle size and then reduced in size just prior to use. Accordingly, the present invention also provides a kit comprising the following separate components for agglomerating into powder coating compositions for the preparation of powder coatings in a number of different colours:

- at least 7 differently coloured film-forming base components,
- an uncoloured film-forming component that is compatible with the coloured film-forming base components and remains compatible therewith during film-formation and that has a Dv.99 of more than 40μm and preferably of no more than 90μm, and

- an uncoloured film-forming component that is incompatible with the coloured film-forming base components or that becomes incompatible therewith during film-formation and that has a Dv.99 of more than 40μm and preferably of no more than 90μm.

In one embodiment of the present invention, the individual particulate components of the powder coating composition comprise

- two or more coloured film-forming base components having a Dv.99 of no more than 30μm, and
- one or more uncoloured film-forming components, at least one component having a higher Dv.99, of more than 20μm and no more than 90μm,

the ratio of coloured film-forming base components to uncoloured film-forming component(s) in the composition being in the range of from 1:99 to 30:70 by weight.

Preferably, the uncoloured film-forming component or at least one, and advantageously all, of the uncoloured film-forming components has a Dv.99 of at least 30μm, more especially at least 35μm, and advantageously at least 40μm. An uncoloured film-forming component having a Dv.50 of at least 8μm and up to 35μm, e.g. up to 30μm, and/or having a Dv.90 of at least 14μm and one having a Dv.90 of no more than 75μm should especially be mentioned.

In a different embodiment of the present invention, the individual particulate components of the powder coating composition comprise

- two or more coloured film-forming base components having a Dv.99 of no more than 30μm, and
- one or more uncoloured film-forming components, at least one component having a higher Dv.99, of more than 40μm and no more than 90μm,

the ratio of coloured film-forming base components to uncoloured film-forming component(s) in the composition being in the range of from 1:99 to 60:40 by weight.

An uncoloured film-forming component having a Dv.50 of at least 10μm and up to 35μm, e.g. in the range of from 12 to 30μm, and/or having a Dv.90 of at least 18μm and one having a Dv.90 of no more than 75μm should especially be mentioned.

A powder coating composition of the invention will in general be a thermosetting system, although thermoplastic systems (based, for example, on polyamides) can in principle be used instead.

When a thermosetting resin is used, the solid polymeric binder system generally includes a solid curing agent for the thermosetting resin; alternatively two co-reactive film-forming thermosetting resins may be used. Thus, a thermosetting powder coating composition according to the invention may contain one or more film-forming polymers selected from carboxy-functional polyester resins, hydroxy-functional polyester resins, epoxy resins, and functional acrylic resins. Carboxy-functional polyester resins should especially be mentioned.

A carboxy-functional polyester film-forming resin may be used, for example, with a polyepoxide curing agent. Such carboxy-functional polyester systems are currently the most widely used powder coatings materials. The polyester generally has an acid value in the range 10-100, a number average molecular weight Mn of 1,500 to 10,000 and a glass transition temperature Tg of from 30°C to 85°C, preferably at least 40°C. The poly-epoxide can, for example, be a low molecular weight epoxy compound such as triglycidyl isocyanurate (TGIC), a compound such as diglycidyl terephthalate condensed glycidyl ether of bisphenol A or a light-stable epoxy resin. Such a carboxy-functional polyester film-forming resin can alternatively be used with a bis(beta-hydroxyalkylamide) curing agent such as tetrakis(2-hydroxyethyl) adipamide.

Alternatively, a hydroxy-functional polyester can be used with a blocked isocyanate-functional curing agent or an amine-formaldehyde condensate such as, for example, a melamine resin, a urea-formaldehye resin, or a glycol ural formaldehye resin, for example the material "Powderlink 1174" supplied by the Cyanamid Company, or hexahydroxymethyl melamine. A blocked isocyanate curing agent for a hydroxy-functional polyester may, for example, be internally blocked, such as the uret dione type, or may be of the caprolactam-blocked type, for example isopherone diisocyanate.

As a further possibility, an epoxy resin can be used with an amine-functional curing agent such as, for example, dicyandiamide. Instead of an amine-functional curing agent for an epoxy resin, a phenolic material may be used, preferably a material formed by reaction of epichlorohydrin with an excess of bisphenol A (that is to say, a polyphenol made by adducting bisphenol A and an epoxy resin). A functional acrylic resin, for example a carboxy-, hydroxy- or epoxy-functional resin can be used with an appropriate curing agent.

Mixtures of film-forming polymers can be used; for example a carboxy-functional polyester can be used with a carboxy-functional acrylic resin and a curing agent such as a bis(beta-hydroxyalkylamide) which serves to cure both polymers. As further possibilities, for mixed binder systems, a carboxy-, hydroxy- or epoxy-functional acrylic resin may be used with an epoxy resin or a polyester resin (carboxy- or hydroxy-functional). Such resin combinations may be selected so as to be co-curing, for example a carboxy-functional acrylic resin co-cured with an epoxy resin, or a carboxy-functional polyester co-cured with a glycidyl-functional acrylic resin. More usually, however, such mixed binder systems are formulated so as to be cured with a single curing agent (for example, use of a blocked isocyanate to cure a hydroxy-functional acrylic resin and a hydroxy-functional polyester). Another preferred formulation involves the use of a different curing agent for each binder of a mixture of two

polymeric binders (for example, an amine-cured epoxy resin used in conjunction with a blocked isocyanate-cured hydroxy-functional acrylic resin).

Other film-forming polymers which may be mentioned include functional fluoropolymers, functional fluorochloropolymers and functional fluoroacrylic polymers, each of which may be hydroxy-functional or carboxy-functional, and may be used as the sole film-forming polymer or in conjunction with one or more functional acrylic, polyester and/or epoxy resins, with appropriate curing agents for the functional polymers.

Other curing agents which may be mentioned include epoxy phenol novolacs and epoxy cresol novolacs; isocyanate curing agents blocked with oximes, such as isopherone diisocyanate blocked with methyl ethyl ketoxime, tetramethylene xylene diisocyanate blocked with acetone oxime, and Desmodur W (dicyclohexylmethane diisocyanate curing agent) blocked with methyl ethyl ketoxime; light-stable epoxy resins such as "Santolink LSE 120" supplied by Monsanto; and alicyclic poly-epoxides such as "EHPE-3150" supplied by Daicel.

The function of coatings is of course protective, but appearance is also important, and the film-forming resin and other ingredients are selected so as to provide the desired performance and appearance characteristics. In relation to performance, coatings should generally be durable and exhibit good weatherability, stain or dirt resistance, chemical or solvent resistance and/or corrosion resistance, as well as good mechanical properties, e.g. hardness, flexibility or resistance to mechanical impact; the precise characteristics required will depend on the intended use. The composition must, of course, be capable of forming a coherent film on the substrate, and good flow and levelling of the composition on the substrate are required. Accordingly, the powder coating composition generally also contains one or more performance additives such as, for example, a flow-promoting agent, a plasticiser, a stabiliser, for exampl a stabiliser against UV degradation, an anti-gassing agent, such

as benzoin, or a filler. Such additives are known and standard additives for use in powder coating compositions. Usually, these performance additiv s will be incorporated in any film-forming component before and/or during the extrusion or other homogenisation process, although, if appropriate, any such additive may alternatively be incorporated as a separate component in the agglomeration process.

Mixing and agglomeration methods are described in EP 372860 A and EP 539385 A.

The agglomerate may, for example, be prepared by mechanofusion of a mixture of the individual components, for example by mechanofusion at a temperature in the range of from 60 to 80°C, or by granulation using methanol or other suitable solvent as granulating agent, to produce composite particles that constitute a free-flowing and fluidisable powder.

Good fluidity of the powder is required for purposes of application to the substrate. This fluidity of powders is governed by their particle size, and particle size also controls the application efficiency of a powder; powders with small particles, i.e. significant quantities <10 microns, more especially <5 microns, exhibit poor fluidity and application characteristics.

The present invention also provides a process for the preparation of a powder coating composition of the present invention, which comprises providing the specified two or more coloured film-forming base components and the one or more specified uncoloured film-forming components in the specified proportions, and mixing and agglomerating the components such that the composition is air-fluidisable and can be applied to a substrate by electrostatic spray.

Agglomeration prevents segregation of the constituents during application and handling, which otherwise would occur, for example during the application process itself (because of differential electrostatic charging) or in the attendant recovery and

recycling process (because of differences in particle size and/or particle density) or in transport, causing batch-to-batch variability in the resulting coating.

The composite particles produced may be likened to raspberries with the individual particles of the raspberry (the drupels) bonded to one another, although the "drupels" are of different sizes, and there will of course also be "raspberries" of different composition and different sizes in the powder as a whole. Inspection of a fused agglomerated powder under an electron microscope shows that one particle is bonded to another and that the individual particles in the composites are more rounded than prior to agglomeration. When a conventional powder coating composition is inspected under an electron microscope, however, the powder particles are seen to be sharp-edged or angular, and are seen as separate, distinct particles - they are not fused to one another.

Furthermore, unlike conventional uniformly coloured powder coating compositions, that contain particles of only a single colour (produced by fusion in the melt extruder), powder coating compositions of this invention consist of a mixture of differently coloured particles and uncoloured particles but nevertheless give the appearance of a single colour on application to a substrate.

An agglomerated powder coating composition according to the invention may in principle be applied to a substrate by any suitable process of powder coating technology, for example by electrostatic spray coating, or by fluidised-bed or electrostatic fluidised-bed processes.

After application of the powder coating composition to a substrate, conversion of the resulting adherent particles into a continuous coating (including, where appropriate, curing of the applied composition) may be effected by heat treatment and/or by radiant energy, notably infra-red, ultra-violet or electron beam radiation.

The powder is usually cured on the substrate by the application of heat (the process of stoving), usually for a period of from 5 to 30 minutes and usually at a

temperature in the range of from 150 to 220°C, although temperatures down to 90°C may be used for some resins, especially epoxy resins; the powder particles melt and flow and a film is formed.

The invention also provides a process for forming a coating on a substrate, which comprises applying an agglomerated composition according to the invention to a substrate, for example by an electrostatic spray coating process, and heating the applied composition to melt and fuse the particles and where appropriate cure the coating.

The film may be any suitable thickness. For decorative finishes, film thicknesses as low as 20 microns should be mentioned, but it is more usual for the film thickness to fall within the range 25-120 microns, with common ranges being 30-80 microns for some applications, and 60-120 microns or, more preferably, 60-100 microns for other applications, while film thicknesses of 80-150 microns are less common, but not rare.

The substrate may comprise a metal, a heat-stable plastics material, wood, glass, or a ceramic or textile material. Advantageously, a metal substrate is chemically or mechanically cleaned prior to application of the composition, and is preferably subjected to chemical pre-treatment, for example with iron phosphate, zinc phosphate or chromate. Substrates other than metallic are in general preheated prior to application or, in the case of electrostatic spray application, are pretreated with a material that will aid such application.

The following Examples illustrate the invention:-

EXAMPLES

Preparation of Individual Components

White, black and red coloured film-forming base components and two uncoloured film-forming components were prepared by mixing the following formulations.

Component A - White Powder Coating Composition

Rutile titanium dioxide white pigment	600 g
Carboxylic acid-functional polyester resin	360 g
Bis(beta-hydroxyalkylamide) curing agent	13 g
Benzoin degassing agent	4 g
Flow modifiers	18 g
Surface waxes	5 g

Component B - Black Powder Coating Composition

Carbon Black pigment	175 g
Carboxylic acid-functional polyester resin	772 g
Bis(beta-hydroxyalkylamide) curing agent	27 g
Benzoin degassing agent	4 g
Flow modifiers	18 g
Surface waxes	4 g

Component C - Red Powder Coating Composition

Earth Red iron oxide pigment	125 g
Carboxylic acid-functional polyester resin	650 g
Bis(beta-hydroxyalkylamide) curing agent	24 g
Benzoin degassing agent	2 g
Flow modifiers	18 g
Surface waxes	4 g
Fillers (barytes)	177 g

Component D - Uncoloured Powder Coating Composition

Carboxylic acid-functional polyester resin	650 g
Bis(beta-hydroxyalkylamide) curing agent	24 g
Benzoin degassing agent	2 g
Flow modifiers	18 g
Surface waxes	4 g
Fillers (barytes)	302 g

Component E - Uncoloured Powder Coating Composition for gloss-reduction

Carboxylic acid-functional polyester resin	575 g
Fillers (barytes)	333 g
Benzoin degassing agent	4 g
Surface waxes	4 g
Flow modifiers	18 g
Bis(beta-hydroxyalkylamide) curing agent	65 g

For the coloured components A to C the ingredients were dry mixed and fed to an extruder blender operating at a temperature of 100°C. The extruder produced a sheet of pigmented resin which was ground to a particle size of below 100 μm and milled on a 100 AFG jet-mill (manufacturer Hosakawa Micron) at 6 Bar grinding air pressure and classified at a speed of 7000 rpm. For uncoloured components D and E the procedure was repeated except that the jet-milling was carried out at 3000 rpm.

The particle size of each of the components was measured on the Malvern Mastersizer X laser light-scattering device from Malvern Instruments.

The particle size distribution for Components A, B and C was:

Dv.50 = 3.5μm

Dv.90 = 5.9μm

Dv.99 = 8.2μm

The particle size distribution for components D and E is:

Dv.50 = 18.4μm

Dv.90 = 36.2μm

Dv.99 = 51.0μm

The polyester of Components A to D had an acid value of 18 to 30. The polyester of Component E had an acid value of 40 to 90.

Preparation and Use of Agglomerated Powder Coating Compositions

Example 1

A mixture comprising:

Component A 187.5 g

Component B	16.7 g
Component C	100.0 g
Component D	695.8 g

was blended together in a Henschel FM10 mixture for 30 minutes in total, with a water jacket taking the temperature to 54°C. The agglomerated powder was sieved through a 110μm steel mesh and then electrostatically applied through a Gema PCG-1 corona spray gun onto an aluminium Q panel. This was then stoved at the recommended time and temperature.

A smooth, glossy coating that had a homogeneous dusky pink colour was produced.

Example 2

A composition comprising

Component A	187.5 g
Component B	16.7 g
Component C	100.0 g
Component D	545.8 g
Component E	150.0 g

was agglomerated and applied to a substrate and stoved as in Example 1.

As shown by their acid numbers, the polyester of Component E has a different functionality and hence different gel time from components A to D, and a smooth, matt coating of 30% gloss at 60° angle is produced that has a homogeneous dusky pink colour.

CLAIMS

1. A powder coating composition in which powder particles are an agglomerate of individual particulate components fused or bonded together into composite particles, wherein the individual particulate components comprise

- two or more coloured film-forming base components having a Dv.99 of no more than 30μm, and
- one or more uncoloured film-forming components having a higher Dv.99,

wherein

the specified uncoloured film-forming component(s) have a Dv.99 of more than 20μm and up to 40μm, the ratio of coloured film-forming base components to uncoloured film-forming component(s) in the composition being in the range of from 1:99 to 30:70 by weight, or

the specified uncoloured film-forming component(s) have a Dv.99 of more than 40μm, the ratio of coloured film-forming base components to uncoloured film-forming component(s) in the composition being in the range of from 1:99 to 60:40 by weight.

2. A powder coating composition in which powder particles are an agglomerate of individual particulate components fused or bonded together into composite particles, wherein the individual particulate components comprise

- two or more coloured film-forming base components having a Dv.99 of no more than 30μm, and
- one or more uncoloured film-forming components, at least one component having a higher Dv.99, of more than 20μm and no more than 90μm,

the ratio of coloured film-forming base components to uncoloured film-forming component(s) in the composition being in the range of from 1:99 to 30:70 by weight.

3. A powder coating composition as claimed in claim 1 or claim 2, wherein the uncoloured film-forming component or at least one of the uncoloured film-forming components has a Dv.99 of at least 30μm.

4. A powder coating composition as claimed in claim 3, wherein the uncoloured film-forming component or at least one of the uncoloured film-forming components has a Dv.99 of at least 35μm.

5. A powder coating composition as claimed in claim 4, wherein the uncoloured film-forming component or at least one of the uncoloured film-forming components has a Dv.99 of at least 40μm.

6. A powder coating composition in which powder particles are an agglomerate of individual particulate components fused or bonded together into composite particles, wherein the individual particulate components comprise

- two or more coloured film-forming base components having a Dv.99 of no more than 30μm, and
- one or more uncoloured film-forming components, at least one component having a higher Dv.99, of more than 40μm and no more than 90μm,

the ratio of coloured film-forming base components to uncoloured film-forming component(s) in the composition being in the range of from 1:99 to 60:40 by weight.

7. A powder coating composition as claimed in claim 1 or claim 6, wher in the ratio of coloured film-forming base components to uncoloured film-forming component(s) is in the range of from 1:99 to 50:50 by weight.

8. A powder coating composition as claimed in claim 7, wherein the ratio of coloured film-forming base components to uncoloured film-forming component(s) is in the range of from 1:99 to 40:60 by weight.

9. A powder coating composition as claimed in claim 8, wherein the ratio of coloured film-forming base components to uncoloured film-forming component(s) is in the range of from 1:99 to 30:70 by weight.

10. A powder coating composition as claimed in any one of claims 1 to 9, wherein the ratio of coloured film-forming base components to uncoloured film-forming component(s) is in the range of from 5:95 to 30:70.

11. A powder coating composition as claimed in any one of claims 1 to 10, wherein the uncoloured film-forming component or at least one of the uncoloured film-forming components has a Dv.90 of at least 14μm.

12. A powder coating composition as claimed in claim 11, wherein the uncoloured film-forming component or at least one of the uncoloured film-forming components has a Dv.90 of at least 18μm.

13. A powder coating composition as claimed in any one of claims 1 to 12, wherein the uncoloured film-forming component or at least one of th uncoloured film-forming components has a Dv.90 of no more than 75μm.

14. A powder coating composition as claimed in any one of claims 1 to 13, wherein the uncoloured film-forming component or at least one of the uncoloured film-forming components has a Dv.99 in the range of from 50 to 65μm.

15. A powder coating composition as claimed in any one of claims 1 to 14, wherein the uncoloured film-forming component or at least one of the uncoloured film-forming components has a Dv.50 in the range of from 5 to 45μm.

16. A powder coating composition as claimed in claim 15, wherein the uncoloured film-forming component or at least one of the uncoloured film-forming components has a Dv.50 of at least 8μm.

17. A powder coating composition as claimed in claim 16, wherein the uncoloured film-forming component or at least one of the uncoloured film-forming components has a Dv.99 of at least 40μm and a Dv.50 of at least 10μm

18. A powder coating composition as claimed in claim 16 or claim 17, wherein the uncoloured film-forming component or at least one of the uncoloured film-forming components has a Dv.50 in the range of from 12 to 30μm.

19. A powder coating composition as claimed in any one of claims 1 to 18, wherein the coloured film-forming base components have a Dv.99 in the range of from 6 to 25μm.

20. A powder coating composition as claimed in any one of claims 1 to 19, wherein the coloured film-forming base components have a Dv.50 of no more than 18μm.

21. A powder coating composition as claimed in claim 20, wherein the coloured film-forming base components have a Dv.50 of no more than 15μm.

22. A powder coating composition as claimed in claim 21, wherein the coloured film-forming base components have a Dv.50 in the range of from 2 to 12μm.

23. A powder coating composition as claimed in any one of claims 1 to 22, wherein the coloured film-forming base components contain in total from 5 to 70 weight % of pigment, calculated on the total weight of those components.

24. A powder coating composition as claimed in any one of claims 1 to 23, wherein the coloured film-forming base components contain in total from 0.5 to 50 weight % of pigment, calculated on the total weight of the composition.

25. A powder coating composition as claimed in any one of claims 1 to 24, wherein the uncoloured film-forming component or at least one of the uncoloured film-forming components is compatible with the coloured film-forming base components during film-formation.

26. A powder coating composition as claimed in any one of claims 1 to 25, wherein the uncoloured film-forming component or at least one of the uncoloured film-forming components is incompatible with the coloured film-forming base components or becomes incompatible therewith during film-formation.

27. A powder coating composition as claimed in any one of claims 1 to 26, wherein the coloured film-forming base components contain a polyester.

28. A powder coating composition as claimed in claim 26 and claim 27, wherein the uncoloured film-forming component or at least one of the uncoloured film-forming components contains a polyester having a different functionality from the polyester of the coloured film-forming base components.

29. A powder coating composition as claimed in claim 27 or claim 28, which includes an uncoloured film-forming component containing a polyester, that component and the coloured film-forming base components containing different curing agents, one of those being an epoxy curing agent or a co-reactable epoxy resin.

30. A powder coating composition as claimed in any one of claims 1 to 29, wherein the specified uncoloured film-forming component having a higher Dv.99 than the coloured film-forming base components is more than 20% by weight of the composition.

31. A kit comprising the following separate particulate compon nts for agglomerating into powder coating compositions for the preparation of powder coatings in a number of different colours:

- a plurality of differently coloured film-forming base components, each with a Dv.99 of no more than 30μm, and
- one or more uncoloured film-forming components having a higher Dv.99, of more than 40μm.

32. A kit as claimed in claim 31, wherein the uncoloured film-forming component or at least one of the uncoloured film-forming components has a Dv.99 of no more than 90μm.

33. A kit as claimed in claim 31 or claim 32, which includes at least 7 differently coloured film-forming base components.

34. A kit as claimed in any one of claims 31 to 33, which includes an uncoloured film-forming component that is compatible during film-formation with the coloured film-forming base components, and an uncoloured film-forming component that is incompatible with the coloured film-forming base components or that becomes incompatible therewith during film-formation.

35. A kit comprising the following separate particulate components for the manufacture of agglomerated powder coating compositions for the preparation of powder coatings in a number of different colours:

- at least 7 differently coloured film-forming base components,
- an uncoloured film-forming component that is compatible with the coloured film-forming base components and remains compatible during film-formation and that has a Dv.99 of more than 40μm and no more than 90μm, and

- an uncoloured film-forming component that is incompatible with the coloured film-forming base components or that becomes incompatible therewith during film-formation, and that has a Dv.99 of more than 40μm and no more than 90μm.

36. A kit as claimed in claim 35, which includes means for comminution of the coloured film-forming base components to a powder having Dv.99 of no more than 30μm.

37. A kit as claimed in any one of claims 31 to 36, wherein the different components are as specified in any one of claims 11 to 29.

38. A kit as claimed in any one of claims 31 to 37, which includes at least 3 uncoloured film-forming components.

39. A kit as claimed in any one of claims 31 to 38, which includes means for agglomerating the components to produce a fluidisable powder.

40. A process for the preparation of a powder coating composition as claimed in claim 1, which comprises providing the specified two or more coloured film-forming base components and the one or more specified uncoloured film-forming components in the specified proportions, and mixing and agglomerating the components into composite particles such that the composition is air-fluidisable and can be applied to a substrate by electrostatic spray.

41. A process for the preparation of a powder coating composition as claimed in claim 1 from a kit as claimed in claim 35, which comprises comminuting at

least two of the coloured film-forming base components to provide powders having a Dv.99 of no more than 30μm, and mixing and agglomerating the two or more comminuted coloured film-forming base components and at least one of the specified uncoloured film-forming components in the proportions specified in claim 1 to form composite particles, such that the composition is air-fluidisable and can be applied to a substrate by electrostatic spray.

42. A powder coating composition when prepared by a process as claimed in claim 40 or claim 41.

43. A process for forming a coating on a substrate, which comprises applying an agglomerated composition as claimed in any one of claims 1 to 30 or claim 42 to a substrate, and heating the applied composition to form a continuous coating.

44. A substrate coated by a process as claimed in claim 43.

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